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PhD Thesis
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# Preface

The thesis is organized in two parts: the first part puts into context the findings of the PhD in an introductive review; the second part consists of the papers listed below. These will be referred to in the text by their paper number written with the Roman numerals **I-V**.

**I** **Li, X.,** Jin, X., Zhao, N., Angelidaki, I., Zhang, Y. 2017. Efficient treatment of aniline containing wastewater in bipolar membrane microbial electrolysis cell-Fenton system. Water Research, 119, 67-72.

**II** **Li, X.,** Angelidaki, I., Zhang, Y. 2017. Salinity-gradient energy driven microbial electrosynthesis of hydrogen peroxide. Journal of Power Sources, 341, 357-365.

**III** **Li, X.,** Jin, X., Zhao, N., Angelidaki, I., Zhang, Y. 2017. Novel bio-electro-Fenton technology for azo dye wastewater treatment using microbial reverse-electrodialysis electrolysis cell. Bioresource Technology, 228, 322-329.

**IV** **Li, X.,** Angelidaki, I., Zhang, Y. Salinity-gradient energy driven microbial electrosynthesis of value-added chemicals from $CO_2$ reduction. Submitted.

**V** **Li, X.,** Chen, S., Angelidaki, I., Zhang, Y. Bio-Electro-Fenton processes for wastewater treatment: advances and prospects. Submitted.

In this online version of the thesis, paper **I-V** are not included but can be obtained from electronic article databases e.g. via www.orbit.dtu.dk or on request from DTU Environment, Technical University of Denmark, Miljoevej, Building 113, 2800 Kgs. Lyngby, Denmark, info@env.dtu.dk.

In addition, the following publications, not included in this thesis, were also concluded during this PhD study.

**VI** **Li, X.,** Zhang, R., Qian, Y., Angelidaki, I., Zhang, Y. 2017. The impact of anode acclimation strategy on microbial electrolysis cell treating hydrogen fermentation effluent. Bioresource technology, 236, 37-43.

**VII** Jin, X., **Li, X.,** Zhao, N., Angelidaki, I., Zhang, Y., 2017. Bio-electrolytic sensor for rapid monitoring of volatile fatty acids in anaerobic digestion process. Water research, 111, 74-80.

**VIII** Zhao, N., **Li, X.,** Jin, X., Angelidaki, I., Zhang, Y., 2018. Integrated electrochemical-biological process as an alternative mean for ammonia monitoring during anaerobic digestion of organic wastes. Chemosphere, 195, 735-741.

**IX** Nadais H., **Li, X.,** Alves N., Couras C., Andersen, H.R., Angelidaki, I., Zhang, Y., 2018. Bio-Electro-Fenton process for the degradation of Non-Steroidal Anti-Inflammatory Drugs in wastewater. Chemical Engineering Journal, https://doi.org/10.1016/j.cej.2018.01.014.

**X** Jin, X., Zhang, Y., **Li, X.,** Zhao, N., Angelidaki, I. 2017. Microbial electrolytic capture, separation and regeneration of $CO_2$ for biogas upgrading. Environmental Science & Technology, 51, 9371-9378.

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# Summary

Bioelectrochemical systems (BESs) have been emerging as promising sustainable biotechnology for wastewater treatment and production of value-added chemicals (such as $H_2O_2$, acetate, and ethanol). However, BESs still face economic and technical challenges, which need considerable attention for achieving full potential at commercial scale. The main objective of this study was to improve the performance and reduce the cost of BESs for chemicals production and pollutants removal.

Firstly, a novel bipolar membrane microbial electrolysis cell (MEC)-Fenton system was developed for the efficient treatment of aniline wastewater. In such system, $H_2O_2$ was in situ generated at the cathode of MEC, which was simultaneously used as a source of $^{\bullet}OH$ for the degradation of aniline. The aniline was effectively degraded under an applied voltage of 0.5 V with aniline removal efficiency of 97.1±1.2%. Moreover, energy balance demonstrated that the MEC-Fenton system is a promising strategy for removal of persistent organic pollutants from wastewater.

In order to reduce the consumption of applied voltage, a hybrid system of the MEC and reverse electrodialysis (RED) technology was developed, for value-added chemicals production and wastewater treatment, which was named microbial reverse-electrodialysis electrolysis cell (MREC). In the MREC, electrical potential generated by the exoelectrogenic microbes and salinity-gradient energy between seawater and river water were utilized to drive $H_2O_2$ production. Operational parameters such as air flow rate, pH, cathode potential, flow rate of salt and fresh water were investigated. The MREC was further integrated with Fenton system for removal of persistent organic pollutants. This hybrid system has several advantages, such as lower operational costs, lower electrical energy consumption, and higher safety level, which provide an efficient and cost-effective system for the degradation of persistent organic pollutants.

Biological conversion of $CO_2$ to value-added chemicals (e.g., acetate and ethanol) in microbial electrosynthesis (MES) has emerged as an attractive approach to address the energy and environmental concerns caused by the fossil fuels. In this study, we designed an innovative MREC system to achieve efficient $CO_2$ conversion. This work expanded the potential of the MREC as an

efficient technology platform for simultaneous $CO_2$ capture and synthesis of value-added chemicals.

# Dansk sammenfatning

Bioelektrokemiske systemer (BESs) er opstået som lovende bæredygtig bioteknologi som kan anvendes til at behandle spildevand og samtidig producere værdifulde kemikalier (såsom $H_2O_2$, acetat og ethanol). BESs står imidlertid stadig overfor økonomiske og tekniske udfordringer, som kræver betydelig opmærksomhed for at opnå fuldt potentiale i kommerciel skala. Hovedformålet med denne undersøgelse var at forbedre ydeevnen og reducere omkostningerne ved anvendelse af BES teknologier til produktion af kemikalier og fjernelse af forurenende stoffer.

For det første, blev et nyt bipolært membran mikrobiel elektrolysecelle (MEC)-Fenton system udviklet til effektiv behandling af anilin-holdigt spildevand. I et sådant system, bliver $H_2O_2$ produceret in situ i katoden af MEC, som samtidigt blev brugt som kilde til $^{\bullet}OH$ dannelse som var ansvarlig for nedbrydning af anilin. Anilinen blev effektivt nedbrudt under en påført spænding på 0.5V med anilinen fjernelses effektiviteten af 97.1 ± 1.2%. I øvrigt viste energibalance også at MEC-Fenton system er en lovende teknologi for fjernelse af svært nedbrydelige forurenende stoffer i spildevand.

For at reducere forbruget af elektrisk energi blev et hybrid system bestående af MEC og reverse electrodialysis (RED) teknologi udviklet til produktion af værdifulde kemikalier og samtidig spildevandsrensning, som blev benævnt mikrobiel reverse electrodialysis elektrolysecelle (MREC). I MREC, blev et elektrisk potentiale frembragt af eksoelektrogenmikrober og saltkoncentrationsgradient energi mellem havvand og flodvand til at drive $H_2O_2$ produktion. Driftsparametre såsom luftstrømningshastighed, pH, katodepotentiale, strømningshastighed af salt og ferskvand blev undersøgt. MREC blev yderligere integreret med Fenton system til fjernelse af vedholdende organiske forurenende stoffer. Dette hybrid system har flere fordele, såsom lavere driftsomkostninger, lavere elektrisk energiforbrug, og højere sikkerhedsniveau, som giver et effektivt og omkostningseffektivt system til nedbrydning af vedholdende organiske forurenende stoffer.

Biologisk omdannelse af $CO_2$ til værdifulde kemikalier (såsom acetat og ethanol) i mikrobiel elektrosyntese (MES) har vist sig at være en attraktiv tilgang til at løse de energi og miljømæssige problemer, der skyldes afhængigheden af fossile brændstoffer. I dette studie, har vi udviklet en innovativ MREC teknologi for at opnå en effektiv $CO_2$ konvertering. Dette arbejde

udvidede MREC's potentiale som en effektiv teknologiplatform til samtidig $CO_2$ opfangning og syntese af værdifulde kemikalier.

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# Abbreviations

| | |
|---|---|
| BESs | Bioelectrochemical systems |
| MFC | Microbial fuel cell |
| MEC | Microbial electrolysis cell |
| BEF | Bio-electron-Fenton |
| MES | Microbial electrosynthesis |
| MREC | Microbial reverse-electrodialysis cell |
| MDC | Microbial desalination cell |
| COD | Chemical oxygen demand |
| TOC | Total organic carbon |
| RED | Reverse electrodialysis |
| MRC | Microbial reverse-electrodialysis cell |
| MRCC | Microbial reverse-electrodialysis chemical production cell |
| MRMC | Microbial reverse-electrodialysis methanogenesis cell |
| AEM | Anion exchange membrane |
| CEM | Cation exchange membrane |
| PEM | Proton exchange membrane |

# 1 Introduction

## 1.1 Background

Bioelectrochemical systems (BESs) are potentially attractive technology for wastewater treatment and value-added chemicals and biofuels production, which utilize electrochemically active bacteria to degrade organic matters in anode chamber and produce a wide range of value-added chemicals and biofuels in cathode chamber, such as $H_2$, $H_2O_2$, acetate, ethanol, butyrate, formic acid and butanol (Bajracharya et al., 2016; Butti et al., 2016; Kumar et al., 2017). Recently, BESs have gained more attention. Various bioelectrochemical technologies have diverse applications. Depending on the application area and configuration of BESs, which are differentiated into microbial fuel cell (MFC, for converting chemical energy to electrical energy) (Du et al., 2007; Hindatu et al., 2017; Saba et al., 2017), microbial electrolysis cell (MEC, for wastewater treatment and $H_2$ production at low applied voltage) (Kitching et al., 2017; Zhang & Angelidaki, 2014), microbial electrosynthesis (MES, for value-added chemicals and biofuels production from $CO_2$) (Aryal et al., 2017a; Schlager et al., 2017; Shin et al., 2017), microbial reverse-electrodialysis cell (MREC, for chemicals production without external power supply) (Kim & Logan, 2011a; Nam et al., 2012; Zhu et al., 2014), bio-electron-Fenton technology (BEF, integrated BESs and Fenton process for bio-refractory pollutants removal) (Olvera-Vargas et al., 2017) and other kinds of BESs (eg., microbial desalination cell (MDC), microbial solar cell (MSC)) (Bajracharya et al., 2016; Schröder et al., 2015).

Wastewater treatment is one of the important applications of BESs. MFC and MEC are the most studied types of BESs. Apart from wastewater can be treated, electrical energy can be generated in MFCs and $H_2$ can be produced in MECs. MEC is an electrical driven BES, derived from MFC, which is originally developed for wastewater treatment and $H_2$ production (Zhang & Angelidaki, 2014). Organic matters in wastewater were oxidized by microorganisms at the anode to generate electrons and protons, $H_2$ was produced in cathode using catalyst by applying a low extra voltage (0.2-0.8 V) (Logan et al., 2008). Compared with traditional biological $H_2$ production technologies, MEC can overcome thermodynamic limitation and obtain high yield $H_2$ production from a variety of organic waste. The fast developing application potential of MEC makes it promising perspectives. Apart from $H_2$ production, $H_2O_2$, $CH_4$ and other value-added chemicals and biofuels (e.g.,

fatty acids and alcohols) also can be simultaneously produced through redox reactions using specific catalyst at the cathode of MEC (Kadier et al., 2016).

$H_2O_2$ as an important industrial chemical was used widely in advance oxidation processes (e.g., Fenton process) for wastewater treatment. Because it has a high content of active oxygen and only water as by-product, was considered a highly efficient and green oxidant (Wang et al., 2016a; Yi et al., 2016). MFC and MEC are able to produce $H_2O_2$ from biodegradable organic wastewater through two electrons reduction of oxygen to $H_2O_2$ on the cathode (Sim et al., 2015b). All MFCs and MECs share one similar principle in anode chamber, in which a wide range of biodegradable organic matters can be oxidized and release electrons, such as acetate, butyrate, propionate, starch, glucose, molasses, cellulose, protein etc. (Escapa et al., 2016; Kadier et al., 2014; Pant et al., 2010). Some complex wastewaters were also could be treated in MFCs and MECs, such as domestic wastewater, fermentation effluent (Marone et al., 2017), swine wastewater (Wagner et al., 2009), refinery wastewater, landfill leachate (Pandey et al., 2016; Puig et al., 2011) etc. However, non-biodegradable and toxic pollutants could not be degraded efficiently by the electrogenic bacteria in the anode chamber, such as aniline, azo dye and pharmaceutical wastewater (Wang et al., 2015). Fenton process has been recognized as an attractive method for bio-refractory organic pollutants degradation due to its high efficiency (Moreira et al., 2017). $H_2O_2$ as one Fenton reaction reagent can be produced through two-electron reduction of oxygen in cathode chamber of MFC and MEC (Chen et al., 2015; Miran et al., 2017). The perspectives of sustainable and cost-effective $H_2O_2$ production in MFCs and MECs offer a potential platform technology for bio-refractory pollutants contained wastewater treatment by integrating Fenton process and MFC or MEC. Hence, recently MFC and MEC have been integrated with Fenton process known as BEF system (Birjandi et al., 2016c; Xu et al., 2013a), such as MFC-Fenton and MEC-Fenton system, which have been demonstrated as promising alternative and cost-effective method for degradation of biodegradable organic pollutants and bio-refractory pollutants (Birjandi et al., 2016a; Ling et al., 2016).

Theoretically, the $H_2O_2$ could be produced in the cathode chamber of MFC. However, the yield of $H_2O_2$ by the MFC is relatively low at low current, only 79 to 196 mg $L^{-1}$ (Chen et al., 2014; Fu et al., 2010a; Fu et al., 2010b; Li et al., 2016a). Comparatively, the maximum concentration could reach to 1300-3100 mg $L^{-1}$ in MEC by applying a low voltage (Arends et al., 2014; Rozendal et al., 2009). Therefore, MEC-Fenton system may be more suitable

technology compared to MFC-Fenton system (Zhang et al., 2015b). Though promising, there are still some challenges need to be addressed before commercial application. For instance, high treatment efficiency was only achieved with synthetic wastewater with a low concentration of pollutants, and the performance would become worse in practical wastewater treatment. Therefore, an efficient BEF system, which can treat real wastewater containing high concentration pollutant, needed to be developed.

In the past decade, many BESs studies are now focusing on fatty acids and alcohols production from $CO_2$ with wastewater treatment, this kind of BES were named MES (Rabaey & Rozendal, 2010; Sadhukhan et al., 2016). In MES, electricity-driven $CO_2$ conversion to value-added chemicals and biofuels using microorganisms as biocatalysts at cathode. However, this technology is still in its infancy period and poses various challenges towards up-scaling and widespread applications, such as low production rate and yield and low catalytic capacity (May et al., 2016). In addition, the high electrical energy required by MES also added the costs to the $CO_2$-to-value chemicals bioconversion process (Christodoulou & Velasquez-Orta, 2016). If electrical energy is derived from renewable and sustainable energy, such as solar, wind or salinity gradients, MES would be a sustainable approach for $CO_2$ conversion to valuable chemicals and wastewater treatment (Luo et al., 2014).

Recently, a novel hybrid BES called Microbial reverse-electrodialysis cell (MREC), which combines a reverse electrodialysis stack (RED) with MEC have been developed to drive $H_2$ or $CH_4$ generation without external power supply (Kim & Logan, 2011a; Logan & Elimelech, 2012; Luo et al., 2014). In MREC, RED was placed between the anode and cathode chamber of MEC, which directly convert the salinity gradient energy from two different concentration solutions (*e.g.*, seawater and river water) into electrical energy, so that replace external power supply to drive MEC. In this context, MREC could be an alternative and efficient platform technology for cost-effective and efficient $H_2O_2$ production and conversion of $CO_2$-to-valuable chemicals without external power supply, which has never been reported by before research. This hypothesis would greatly expand the range of MREC potential applications for conversion of $CO_2$-to-value-added chemicals and biofuels. Therefore, it is meaningful to explore the feasibility of MREC in value-added chemicals and biofuels production.

## 1.2 Objectives and thesis structure

### 1.2.1 Specific objectives

The key objective of this PhD project was to research and develop new BESs (MEC and MREC) for $H_2O_2$ production and wastewater treatment, so that improve the treatment efficiency of BESs on wastewater containing high concentration of bio-refractory organic pollutants, and reduce the cost of wastewater treatment. Moreover, develop the MREC technology to produce value-added chemicals and biofuels from $CO_2$ and with simultaneous wastewater treatment.

Specific objects are:

- Development of an innovative and cost-effective BEF technology for wastewater treatment. (**Paper I and Paper III**)
- Development of a novel MES system for production of commodity chemicals. (**Paper II and Paper IV**)
- Reduce the cost of BEF system for wastewater treatment. (**Paper I and Paper III**)
- Development of the hybrid system of RED and BESs application on $H_2O_2$ production. (**Paper II**)
- Development of the hybrid system of RED and BESs application on degradation of bio-refractory pollutants. (**Paper III**)
- Development of the hybrid system of RED and BESs for $CO_2$ conversion to value-added chemicals and biofuels. (**Paper IV**)
- Reduce the electrical energy consumption of MES for acetate synthesis from $CO_2$ reduction. (**Paper IV**)

### 1.2.2 Structure of the thesis

In chapter 2, a state-of-the-art overview of the BESs on the $H_2O_2$ production and degradation of bio-refractory pollutants, especially with respect to the treatment performance associated with reactor design and main operating parameters are described. An innovative MEC-Fenton system with bipolar membrane was developed to treat real aniline wastewater. The effect of key operating parameters such as wastewater pH, external applied voltage, and air flow rate were described. In addition, the energy efficiency of this system for aniline removal was also evaluated. (**Paper I**)

In chapter 3, a state-of-the-art overview of hybrid systems of BESs and RED. The MREC system was developed to produce $H_2O_2$ and treat azo dye wastewater. The effect of key operating parameters such as wastewater pH, cathode potential, initial azo dye concentration and the air flow rate were described. In addition, the capital costs and energy consumption of this system for azo dye removal were evaluated. (**Paper II and Paper III**)

In chapter 4, an innovative microbial reverse-electrodialysis synthesis cell (MRESC) system was developed to synthesize acetate and ethanol from $CO_2$ reduction. The effect of key operating parameters such as flow rate of seawater and river water, $CO_2$ feeding rate, and salinity ratio were investigated. Furthermore, the wastewater treatment efficiency in the anode chamber of MRESC was evaluated. (**Paper IV**).

# 2 BESs for $H_2O_2$ production and wastewater treatment

The biodegradable organic waste could be easily degraded through bacterial oxidation in the anode chamber of BESs. However, bio-refractory pollutants cannot be degraded by the microorganisms that grown at the anode (Hassan et al., 2017a; Santoro et al., 2017; Zhuang et al., 2010a; Zhuang et al., 2010b). Fenton process as one of the typical advanced oxidation processes is an effective method to completely oxidize persistent organic pollutants in wastewater by highly oxidative hydroxyl radicals ($^{\bullet}OH$) formed from the reaction of $H_2O_2$ with $Fe^{2+}$ (Gligorovski et al., 2015). BES has been demonstrated as an alternative technology to produce $H_2O_2$ in cathode chamber (Asghar et al., 2014). So, integrating BESs and Fenton process could be an ideal technology to remove biodegradable and persistent organic pollutants. The combining process was named as BEF system and has received increasing attention in recent years resulting in the fast development of a series of BEF systems.

In order to obtain high degradation performance of pollutants in BEF systems, high $H_2O_2$ production rate and yield are necessary (Zhang et al., 2015b). To attain high $H_2O_2$ production rate, the contact of cathode, catholyte and oxygen must be maximized. For this reason, BESs reactor construction, gas-diffusion electrodes, and three-dimensional electrodes with high surface area were exploited (Chen et al., 2015). BESs have been demonstrated as alternative methods for $H_2O_2$ production, such as MFCs and MECs. In different BES, the optimal $H_2O_2$ production conditions and maximum $H_2O_2$ concentration are obviously different (see table 1). The cathode potential as one key parameter for $H_2O_2$ production on cathode also varied in different BESs. Sim et al. (2015b) found that the maximum $H_2O_2$ concentration can be obtained at cathode potential of -0.4 V. However, Chen et al. (2015) find the maximum $H_2O_2$ concentration of 711.2 mg $L^{-1}$ was achieved under the cathode potential of -0.85 V with 0.5 V applied voltage in MEC. It was also found in Miran et al. study (2017) that the optimal external voltage was 0.4 V in MEC for $H_2O_2$ production.

In general, the BEF system consists of two chambers separated by a membrane (e.g., proton exchange membrane (PEM) or anion exchange membrane (AEM) or cation exchange membrane (CEM)). The anaerobic anode is filled with wastewater containing biodegradable waste while the aerobic cathode

chamber is filled with wastewater containing bio-refractory pollutants (Zhu & Ni, 2009). Nearly all BEF systems share one common principle in the anode chamber, in which biodegradable organic matters are oxidized by microorganisms. The electrons are released from the oxidation processes (Eq. 1) and transported to the cathode through external circuit. The bio-refractory pollutants removal processes mainly occur in the cathode chamber. The two-electron reduction of oxygen on the cathode results in $H_2O_2$ formation (Eq. 2) which then reacts with $Fe^{2+}$ to produce $^{\bullet}OH$ (Eq. 3) for pollutants oxidation (Feng et al., 2010).

**Table 1.** Performance of $H_2O_2$ production in different BESs.

| METs | Cathode | External voltage | Cathode potential | $H_2O_2$ yield (mg $L^{-1}$) | Reference |
|---|---|---|---|---|---|
| MFC | Graphite rod | - | -0.25 V | 78.85 | (Fu et al., 2010b) |
| MFC | Graphite | - | - | 196.5 | (Chen et al., 2014) |
| MFC | Carbon felt | a | -0.2 V | ~0.68 | (Milner et al., 2017) |
| MFC | Graphite felt | - | - | ~13 | (Wang et al., 2017a) |
| MFC | Graphene oxide | - | -0.4 V | 273 | (Dong et al., 2017) |
| MEC | Graphite | 0.5 V | - | ~1300 | (Rozendal et al., 2009) |
| MEC | Graphite | b | - | 439 | (Zhang et al., 2015c) |
| MEC | Graphite | 0.5 V | -0.85 V | 711.2 | (Chen et al., 2015) |
| MEC | Graphite | a | -1.7 V | 1447 | (Sim et al., 2015) |
| MEC | Graphite | c | - | 700 | (Modin & Fukushi, 2013) |
| MEC | Air cathode | d | - | 3100 | (Young et al., 2016) |
| MEC | Air cathode | d | - | 3100±370 | (Young et al., 2017) |
| MEC | Carbon cloth | - | -0.5 V | 230 | (Ki et al., 2017) |

a: Control the cathode potential using potentiostat. The potentials were vs. Ag/AgCl reference electrode.
b: MFC power the MEC.
c: Control the current by a potentiostat.
d: Control the anode potential using potentiostat.
-: No report in reference

$$C_xH_yO_z + (2x - z)H_2O \rightarrow x\,CO_2 + (4x + y - 2z)H^+ + (4x + y - 2z)e^- \quad (1)$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (2)$$

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + {}^{\bullet}OH + H_2O \quad (3)$$

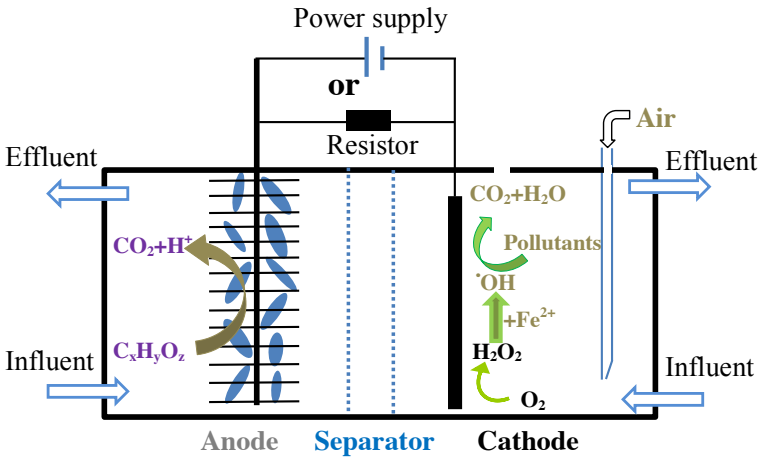


**Figure 1.** Schematic of BEF systems for wastewater treatment. Based on the different structures, most BEF systems can be broadly classified into MFC-Fenton system and MEC-Fenton system. (Separator: CEM, AEM, PEM).

## 2.1 MFC-Fenton system

MFC is a device that using electroactive bacterial as biocatalysts to degrade organic matters in the anode chamber and release electrons, the electrons were transferred to the cathode via external circuit, thereby generating current. Recently, MFC was demonstrated as one alternative method to produce $H_2O_2$ through two electrons reduction of oxygen without external power supply. Therefore, integrating MFC and Fenton process could be an ideal technology to treat wastewater containing bio-refractory pollutants. The first MFC-Fenton system was reported by Zhu and Ni in 2009 (Zhu & Ni, 2009), it is a very young technology.

### 2.1.1 Application of MFC-Fenton system

So far, the MFC-Fenton system is the most studied type BEF systems. MFC-Fenton systems are being developed for removal of bio-refractory pollutants from wastewater with the purpose of aquatic environment protection. In accordance with this classification, the degradation behavior of dyestuffs, pharmaceuticals and some other industrial pollutants are described in below.

**Azo dyes**, which constitute an important portion of wastewater effluent, most are bio-refractory and high persistence in soils and aquatic systems. The azo dyes have been demonstrated decolorized completely in classical MFC (Mu et al., 2009; Solanki et al., 2013) and MFC-MEC coupled systems (Li et al., 2016b). However, the color disappearing was only due to the cleavage of azo bond, the mineralization was not as efficient as that of depolarization. For example, in MFC, the methyl orange could be cleaved into sulfanilic acid and

N, N-dimethyl-p-phenylenediamine (Liu et al., 2009) or *N*, *N*-dimethylaniline and sodium sulfanilate (Li et al., 2016b). These by-products still are not friendly to the environment. In MFC-Fenton system, the azo dyes could be degraded and mineralized completely, such as methylene blue, orange G, lissamine green B, crystal violet, orange II, amaranth and so on. Moreover, since some azo dyes could also be used as electron acceptors in the cathode, *e*.*g*., Acid Orange 7 (Mu et al., 2009), the current density would increase with the increasing of azo dyes concentration during the decolorize stage. Higher current density would be beneficial for the degradation of azo dyes. In addition, higher organic contents would lead to higher current efficiency with smaller energy consumption but requiring a longer time for attaining acceptable mineralization degrees (Asghar et al., 2014).

**Pharmaceutical wastewater** is typically co-treated with municipal wastewater and it is responsible for a significant input of pharmaceuticals into wastewater treatment plants (Casas et al., 2015; Svojitka et al., 2017). Conventional wastewater treatment plants provide inefficient removal because of some pharmaceuticals usually resistant to biodegradation (Birjandi et al., 2016b; Brillas et al., 2009). In the past years, MFC-Fenton systems have been widely used for pharmaceutical removal. Several pharmaceutical pollutants such as 17β-estradiol, 17α-ethynyl-estradiol, sulfadimidine, paracetamol (Zhang et al., 2015a) and estrone have been demonstrated for their removal in the MFC-Fenton systems. For instance, Xu et al. (2013b) demonstrated 81% of 17β-estradiol and 56% of 17α-ethynyl-estradiol removal in MFC-Fenton system. The external resistance was the key factor in 17β-estradiol removal. When the external resistance was equal to the internal resistance of the system, 17β-estradiol removal could reach over 90% under various pH values (2-7) of the pharmaceutical wastewater (Xu et al., 2015). The removal of estrone and sulfadimidine in MFC-Fenton system also has been demonstrated (Yuan et al., 2017). In continuous mode, the removal efficiencies for estrone and sulfadimidine could reach 100% and 97%, respectively. Real medicinal herbs wastewater treatment has also been investigated using MFC-Fenton system. The maximum COD removal of 84.02% was achieved under optimal conditions (Birjandi et al., 2016b).

**P-nitrophenol** is widely used in the manufacturing of pesticides, pharmaceuticals, herbicides, explosives, dyes and other chemical industries (Zhang et al., 2012). Considering the toxicity and carcinogenicity of p-nitrophenol, the p-nitrophenol contained wastewater is categorized as hazardous waste. The MFC-Fenton process has been applied to remove the p-nitrophenol attributing

to the oxidation by $^{\bullet}OH$ (Feng et al., 2011; Tao et al., 2013; Zhu & Ni, 2009). The p-nitrophenol was firstly degraded into carboxyl acids, and then completely mineralized into $H_2O$ and $CO_2$ (Zhu & Ni, 2009). When using the limonite as the $Fe^{2+}$ source, the iron resource cost was only 0.03 Euro per Kg $L^{-1}$ p-nitrophenol (Tao et al., 2013).

**Landfill leachate** can reach the adjacent surface and groundwater, which could cause potentially serious hazards to the surrounding environment and public human health (Hassan et al., 2017b). When landfill leachate was used as an anodic substrate in MFC, the treatment efficiency and COD removal of landfill leachate were quite low owing to a huge portion of persistent organic pollutants (Pandey et al., 2016). Ganesh and Jambeck (Ganesh & Jambeck, 2013) applied MFC treat landfill leachate with 12033 ± 3974 mg $L^{-1}$ COD, the COD removal only was 28%. When MFC-Fenton system was applied to treat landfill leachate (Li et al., 2010). The color and COD removal efficiency could reach to 77% and 78%, respectively. The treatment performance in MFC-Fenton system is better that of MFC. As no commercial extra reagent was needed, this process was low cost and high effective. Most recently, MFC-Fenton system was evaluated as post-treatment of an anammox system to treat landfill leachate (Hassan et al., 2017a; Hassan et al., 2017b), the effluent with COD of 2401 ± 562 mg $L^{-1}$ from anammox reactor were fed in anode and cathode chamber, a maximum COD removal rate of 1077 ± 60 mg $L^{-1}d^{-1}$ with COD removal of 65% was achieved. These results demonstrated that the MFC-Fenton system integrated with conventional techniques will have practicable value in the engineering application.

**Swine wastewater** is one kind of biodegradable wastewater, which could be biodegraded in anode chamber of MFC (Kadier et al., 2014b). However, the pollutants in swine wastewater could not be completely degraded in the anode chamber. Xu et al. (2011) investigated the anodic biodegradation and cathodic Fenton process for enhanced swine wastewater treatment in MFC-Fenton system. In their study, real swine wastewater with COD of 1652 mg $L^{-1}$, $NH_3$-N of 378 mg $L^{-1}$ and $BOD_5$ of 372 mg $L^{-1}$ was first treated in the anode chamber, where 46.5% of COD, 58.7% of $NH_3$-N, 71.7% of $BOD_5$ and 38.4% of TOC were removed. Subsequently, the anode effluent was transferred into the cathode chamber, where the COD, $NH_3$-N, $BOD_5$ and TOC removal could reach to 76.7%, 88.5%, 92.3% and 95.7%, respectively.

### 2.1.2 Factors affecting the MFC-Fenton performance

The degradation efficiency of organic pollutants in MFC-Fenton systems depends on operation parameters such as wastewater pH, cathode material, air

flow rate, cathode potential and initial pollutants concentration. Most of these parameters need to be optimized for achieving the best removal efficiency and lowest energy cost.

**The wastewater pH** is the most important operation parameters in Fenton reaction. In the MFC-Fenton process, it has been found that acidic pH (2-3) is important for removal of bio-refractory pollutants in the cathode chamber. At high pH ($\geqslant$4), the formation of $Fe(OH)_2/Fe(OH)_3$ would lead to the catalyst deactivation, which decreases the quantity of $^{\bullet}OH$ (Moreira et al., 2017). Thus, it requires an initial pH adjustment with acids and final neutralization of the treated wastewater before it is released into the environment. However, when the pH is lower than 2, the performance of pollutants removal also would be inhibited. It could be due to the reaction of $H_2O_2$ with excessive $H^+$ to generate $H_3O_2^+$, which is difficult to react with $Fe^{2+}$ to generate $^{\bullet}OH$. Due to the consumption of $H^+$ at cathode, the pH of wastewater in cathode chamber would increase to over 7 with the Fenton reaction, if no extra pH control was implemented.

**The cathode material** is one of the most important parts of MFC-Fenton system. The distinct advantages of MFC-Fenton systems are the in situ production of $H_2O_2$ via the oxygen reduction reaction and the pollutants degradation at the cathode. Among the MFC-Fenton systems, $H_2O_2$ generation plays a decisive role and is affected by the types and properties of cathode materials (Zhao et al., 2016). To improve the cathode reaction activity, various carbonaceous materials have been widely investigated as cathodes, such as carbon felt (Tao et al., 2013; Zhu & Ni, 2009), graphite (Fu et al., 2010b; Zhang et al., 2015b), gas-diffusion electrodes (Rozendal et al., 2009) and so on. The carbon-felt has a high specific surface that favors the fast generation of both components of the Fenton's reagent, and then $^{\bullet}OH$ is produced from Fenton's reaction without significant $H_2O_2$ accumulation. Graphite possesses a large number of active surface sites leading to a very fast oxygen reduction and accumulation $H_2O_2$. Some of the key drawbacks of classical Fenton process are the use of amounts of iron with further formation of iron sludge that must be removed and properly treated at the end of Fenton process, and need of acidification and subsequent neutralization (Moreira et al., 2017). Recently, composite cathodes based MFC-Fenton systems has attracted increasing attention due to its merits on $H_2O_2$ productivity and efficient Fenton activity. This type of processes extends the acceptable pH range and increases the efficiency of $^{\bullet}OH$ generation. For example, CNT/γ-FeOOH (Fu et al., 2010b), $Fe@Fe_2O_3$/carbon felt (Xu et al., 2011), $Fe@Fe_2O_3$/NCF (Xu et al., 2013),

Carbon felt/γ-FeOOH (Wang et al., 2014), $Fe_2O_3$/active carbon felt (Ling et al., 2016) and Fe@$Fe_2O_3$/graphite (Yong et al., 2017) have been successfully used as cathode to degrade bio-refractory pollutants at neutral pH. These materials could serve as a solid $Fe^{2+}$ source to avoid any excessive use of acids to adjust pH.

**The initial concentration of pollutants** in wastewater could directly affect the degradation efficiency. Most of MFC-Fenton systems could only obtain high treatment efficiently with low concentration pollutants. Moreover, the increase of initial pollutant concentration always leads to lower degradation efficiency and prolongs the degradation time. The reason for this phenomenon could be the low production yield of $H_2O_2$ and pH increasing with reaction in the cathode chamber, which was insufficient to degrade high concentration pollutants (Asghar et al., 2014; Asghar et al., 2015). However, most industrial wastewaters often contain high concentration pollutants. So, MFC-Fenton systems need to be further developed to treat relatively high concentrations of bio-refractory pollutants before commercial application.

**The cathode potential** is another important operational parameter for removal of pollutants. In the first case, optimized cathode potential is usually chosen to obtain the maximum $H_2O_2$ production rate and concentration, and its value depends on the cathode material. For example, the optimized cathode potentials reported was -0.4 ~ -0.5 V (vs. SCE) for graphite cathode, and -1.6 V (vs. Ag/AgCl) for carbon black graphite hybrid cathode, respectively (Li et al., 2016a). It has been demonstrated that the cathode potential could significantly affect the removal of pollutants. As an example, Fu et al. (2010b) shown that cathode potential of MFC-Fenton system was affected by the external resistance, it would drop rapidly with the degrading of amaranth (Fu et al., 2010b).

**The air flow rate** has been demonstrated as one important parameter for the $H_2O_2$ generation in MFCs. Oxygen is the electron acceptor on the cathode surface for $H_2O_2$ production. Passive $O_2$ diffusion from air to gas diffusion cathode was an energy-saving method to generate $H_2O_2$ in MFCs. However, the mass transport of $O_2$ to the cathode would be limited under passive $O_2$ diffusion conditions, and thus slow down the $H_2O_2$ production rate. To overcome this limitation, the cathode with optimal catalytic activity for $H_2O_2$ production needs to be explored. Commercial carbon and graphite material were widely used in MFC-Fenton systems as cathode due to their low costs and high efficiency for $H_2O_2$ synthesis. In MFC-Fenton systems with carbon or graphite material as the cath-

ode, air is required to be pumped into cathode chamber. High air flow rate could enhance the dissolved oxygen in solution and promote the oxygen mass transfer rate, and thus, is beneficial for $H_2O_2$ production and accumulation. However, extremely high air flow rates are not recommended since they may cause several problems such as excessive air supply could cause a decrease in $H_2O_2$ accumulation (Ling et al., 2016). Meanwhile, the air flow rates could also affect the energy consumption in terms of air gas pumping, and thus, setting an optimal air flow rate is important for the commercial application.

### 2.1.3 Advantages and challenges of MFC-Fenton system

MFC-Fenton process has two key advantages over conventional electro-Fenton and Fenton processes: (1) no requirement of an external power source for the Fenton reaction. The electrons are derived from bacteria at the anode; (2) the utilization of $H_2O_2$ and $Fe^{2+}$ is better than other dosing methods, as the $H_2O_2$ can be in situ generated and rapidly used for generating $^{\bullet}OH$ (Asghar et al., 2014; Asghar et al., 2015). However, there are still some challenges on the removal of pollutants. First, the efficiency of pollutants removal is limited by the pollutants concentration and low current density caused by resistance load of MFC-Fenton system. In general, the low current density may lead to the high current efficiency with less energy consumption but require longer times for obtaining acceptable removal efficiency (Fu et al., 2010b). Moreover, the $H_2O_2$ concentration in MFC is still low, which are insufficient to degrade high concentrations of pollutants (Asghar et al., 2014). The high removal efficiency of pollutants through MFC-Fenton system has only been demonstrated at low concentration pollutants. For instance, 100% degradation efficiency was obtained with 25 mg $L^{-1}$ amaranth azo dye, while the degradation efficiency decreased to 75.65% when the concentration of amaranth increased to 75 mg $L^{-1}$ (Fu et al., 2010b). Tao et al. (2013) also found the removal efficiency of p-nitrophenol decreased from 96% to 63% with the concentration increasing from 0.25 mM to 25 mM. Fernandez et al. (2013) reported maximum mineralization efficiency of 82% and 70% for 10 mg $L^{-1}$ of Lissamine Green B and 10 mg $L^{-1}$ of crystal violet dye, respectively. Furthermore, most of MFC-Fenton studies only focus on the batch operation mode. However, from the engineering point of view, continuous feeding of the wastewater in MFC-Fenton system is needed (Asghar et al., 2014).

## 2.2 MEC-Fenton system

MECs with aerobic cathode have been demonstrated as more efficient method for $H_2O_2$ production compared with MFCs (Chen et al., 2015; Rozendal et al.,

2009). Although MECs require a small amount of electricity supply (0.3-0.8 V), the $H_2O_2$ production rate and yield are several magnitudes higher than that of MFCs (see Table 1). Therefore, MEC is one more suitable process for $H_2O_2$ generation than MFC. Thus, MEC-Fenton system could be applied for wastewaters containing relatively high concentration pollutants.

### 2.2.1 Application of MEC-Fenton system

Aniline is widely used in many industries, such as the production of dyes, pharmaceuticals and rubber chemicals. Aniline has the characteristics of long-term residue and carcinogenic properties, which has been listed as priority control pollutant by the U.S. Environmental Protection Agency (Wang et al., 2016b). The aniline containing wastewater is toxic to human beings and could cause potentially serious hazards on the surrounding environment, which must be high efficiency treated before discharge. However, conventional wastewater treatment plants are not able to remove high concentration aniline wastewater. An efficient process that can meet the demand of aniline wastewater treatment is quite valuable. Classical MEC-Fenton system has been demonstrated as one promising alternative and economical method to traditional Electro-Fenton systems for degradation of bio-refractory pollutants (Nadais et al. 2018). In order to address the challenges of classical MEC-Fenton systems, one effective MEC-Fenton system with the bipolar membrane was developed in the **paper I** (see Figure 2), which can treat industrial wastewater without causing pH issues. The bipolar membrane was used to avoid $H^+$ transfer to the anode chamber and maintain the low pH of cathode. The anode and cathode chambers were filled with domestic wastewater and aniline wastewater, respectively.

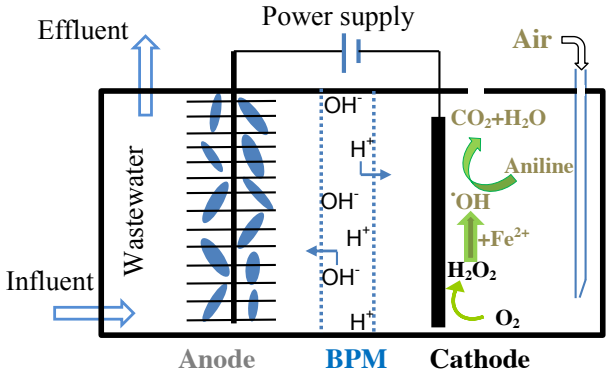


**Figure 2.** Schematic of bipolar membrane (BPM) MEC-Fenton system (**Paper I**).

In order to save the electric energy spent on the MEC-Fenton system, MFC as a renewable power source have been recently utilized to drive the MEC-Fenton system. Zhang et al. (2015b) demonstrated the feasibility of using

MFC to drive the MEC-Fenton system for methylene blue removal. In Zhang's study, the maximum removal efficiency of methylene blue reached to 99.4%. The $H_2O_2$ production and methylene blue degradation performance were improved by connecting 4 MFCs as a power supply. This system has several advantages: (1) electricity can be harvested from MFC without external electrical source; (2) the residual $H_2O_2$ removal as one of the key challenges in Electro-Fenton and Fenton processes, which can be easily removed by switching the operation mode (Zhang et al., 2015b). Nevertheless, several challenges still need to be addressed before commercial application. For example, the pollutant removal rate and current density are still lower than conventional electro-Fenton process. Though the current density and voltage applied to MEC could be enhanced by connecting several MFCs in series, this method may not be feasible for long-term operation due to the voltage reversal (Zhang & Angelidaki, 2014), and the current of MEC could not increase proportionally with the simply connecting MFCs in series (Wang et al., 2011).

### 2.2.1 Factors affecting the MEC-Fenton system performance

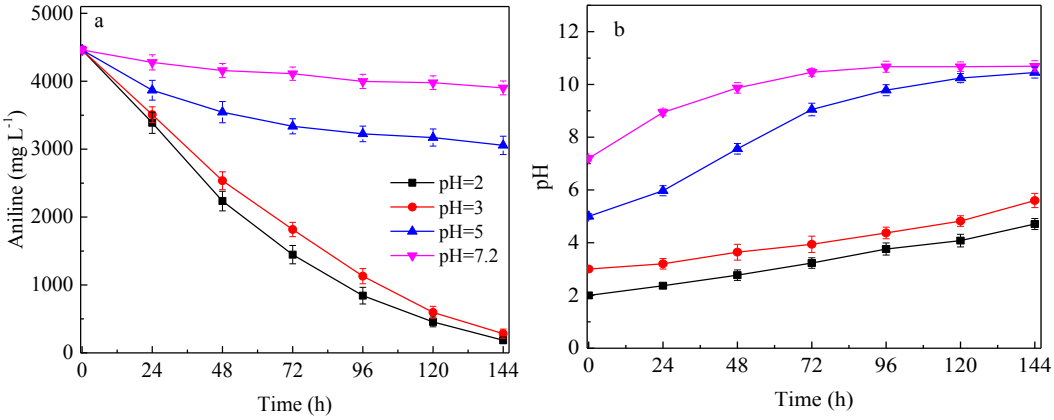


**Figure 3.** The effect of initial pH of wastewater on the degradation of aniline in the MEC-Fenton system (**Paper I**).

**The pH of wastewater** also is one important parameter in MEC-Fenton systems like with MFC-Fenton systems. The influence of initial pH on aniline degradation in MEC-Fenton system was tested in **Paper I**. As shown in Figure 3, the aniline removal only was 8% at native pH (7.2) of aniline wastewater. Comparatively, the aniline removal could be increased with the decreasing of initial pH. When the pH was adjusted to 3, the aniline removal efficiency could be increased to 97.1 ± 1.2%. In Zhang's study (2015b), the optimal pH for methylene blue removal in MEC-Fenton system also was 3. The aniline wastewater pH increased slowly to 5.6 from the initial 3 after 6 days (Figure 3b). However, when the initial pH was set at 7.2, the pH would

be increased to 10.7 after 3 days. When using CEM replaced the bipolar membrane. The removal of aniline was only observed in first 3 days in the MEC-Fenton process with CEM (**Paper I**). The results in the **paper I** demonstrated that the bipolar membrane as a separator in MEC-Fenton system could maintain the catholyte pH at the optimal condition for Electro-Fenton reaction without extra acid dosage when the initial pH was set at 3.

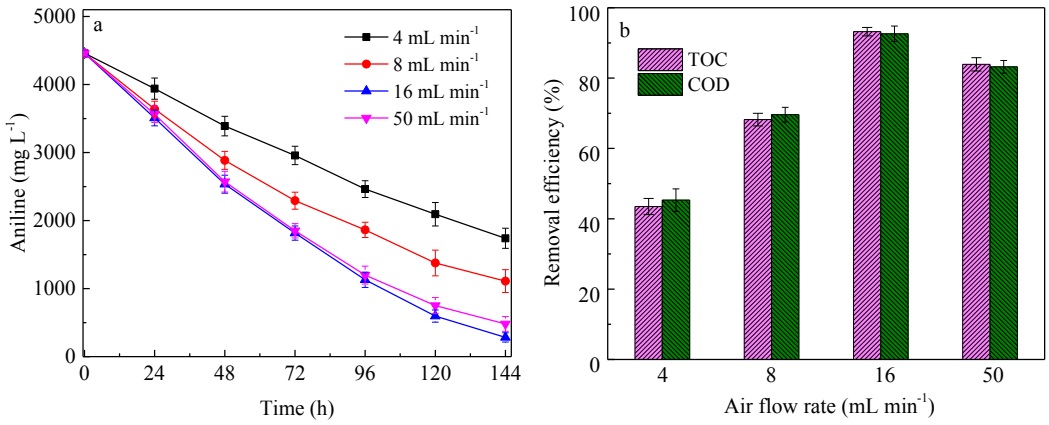


**Figure 4.** Effect of air flow rate on the performance of bipolar membrane MEC-Fenton system (**Paper I**).

**Air flow rate** also could affect the degradation of bio-refractory pollutants in MEC-Fenton system (Nadais et al. 2018). The $H_2O_2$ concentration could reach to 1300 mg $L^{-1}$ with a production rate of 1.9 ± 0.2 kg-$H_2O_2$ $m^{-3}$ $d^{-1}$ in MEC (Rozendal et al., 2009). The energy consumption only was 0.93 kWh $kg^{-1}$-$H_2O_2$. Several studies also demonstrated the passive $O_2$ diffusion using gas diffusion cathode was efficient for $H_2O_2$ production in MECs (Modin & Fukushi, 2013; Sim et al., 2015a). However, it is generally considered that the increasing of dissolved $O_2$ and mass transfer rate in wastewater could improve the $H_2O_2$ production in the cathode chamber of MEC (Ling et al., 2016), and then promoted the Fenton process. For example, in the **paper I**, the removal rate of aniline increased with the increas of air flow rate from 4 to 16 mL $min^{-1}$. Further increase the air flow rate to 50 mL $min^{-1}$, no further increase in the aniline removal was observed. That is because there was a saturated state for dissolved $O_2$ in wastewater, thus the accumulations of $H_2O_2$ hardly increased after dissolved $O_2$ in wastewater was saturated. In addition, high air flow rate could disturb the mass transfer between the electrode and aniline wastewater, and the resistance of the aniline wastewater also increased with the excessive mass of air bubble in the cathode chamber, which could lead the removal efficiency of pollutant did not further increase at higher air flow rate. Similar phenomena were reported in Electro-Fenton sys-

tem (Zhou et al., 2013a; Zhou et al., 2013b). In the bipolar membrane MEC-Fenton system, the mineralization rate increased from 43.5 ± 2.3% to 93.1 ± 1.2% with the increase of air flow rate from 4 to 16 mL $min^{-1}$. When the air flow rate further increased to 50 mL $min^{-1}$, the mineralization rate only was 83.9 ± 1.9% (**Paper I**). These studies indicated that setting an optimum air flow rate in MEC-Fenton system is important for pollutants removal.

**Applied voltage** could enhance the current so that improve the removal efficiency of bio-refractory pollutants in MEC-Fenton system (Nadais et al. 2018). However, the degradation efficiency cannot be increased indefinitely since the cathode potential also would be changed by the increase of applied voltage, resulting in the side reactions, and thereby decreasing current efficiency and pollutants removal efficiency. In the bipolar membrane MEC-Fenton system, aniline removal efficiency could reach to a maximum at 0.5 V (**Figure 5**). Enhancement of the current under optimized cathode potential would be one of the emphases for future research.

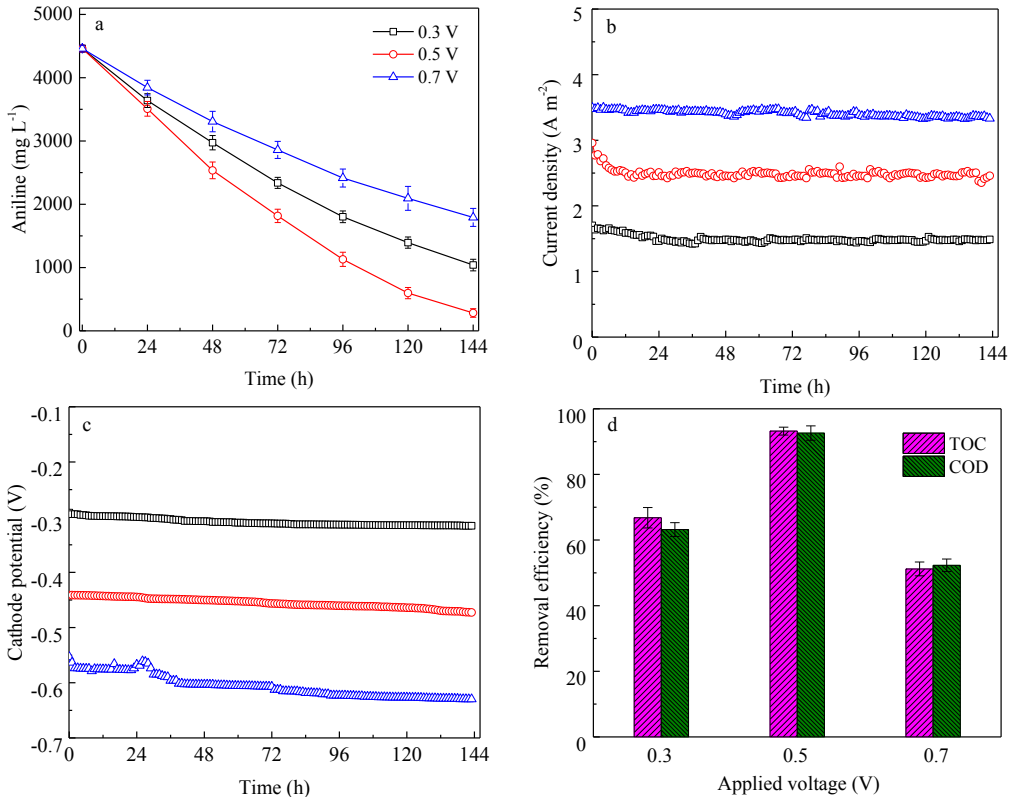


**Figure 5.** The effect of applied voltage on the performance of aniline wastewater treatment (**Paper I**).

### 2.2.2 Advantages and challenges of MEC-Fenton system

Compared with MFC-Fenton system, the MEC-Fenton system has some advantages: (1) could be used to treat wastewater contained with relativly high

concentration bio-refractory pollutants. (2) The current can be enhanced by the application of external power source. The removal rates of bio-refractory pollutants are significantly higher than that in MFC-Fenton system. However, some challenges are still need to be addressed before commercial application. For instance, the pH in the cathode chamber of classical MEC-Fenton system would rise over 7 in short time, which would limit the degradation performance of pollutants. Furthermore, most of the classical MEC-Fenton systems only reported high treatment efficiency on synthetic wastewater with low pollutant concentration (Zhang et al. 2015, Nadais et al. 2018). In practice, many industrial wastewaters often contain high concentration pollutants. It is necessary to evaluate the feasibility of pollutant removal performance of real industrial wastewater in MEC-Fenton system. Finally, MEC-Fenton systems still require an external power supply to drive the Fenton process, only few studies focused on this system in recent years. The development aimed at increasing system performance (e.g., increasing the current by lowering MEC internal resistance and design rational architecture of MEC) should be pursued.

## 2.3 Challenges of the Bio-Electro-Fenton systems

The BEF systems are suitable for the treatment of wastewater containing recalcitrant organic pollutants. Most of the pollutants can be completely oxidized through the process. Although BEF systems are perhaps economical and effective technology, some drawbacks such as the need of acidic condition (e.g., pH=2-3.5) and lower degradation rate of pollutants than that of Fenton and Electro-Fenton process. The other factor that limited the development of larger-scale BEF systems is the cost. The capital and operation costs of BEF systems could be two of the decisive economic factors for commercialization of the technology for wastewater treatment (Zhang & Angelidaki, 2016). However, so far, most studies of BEF systems are only focused on fundamental issues, the capital and operation costs are rarely reported. Therefore, the information of capital and operation costs should be accurately provided, which are also essential to understand the benefits of the BEF systems before commercial application. Furthermore, the MEC-Fenton systems could be one more promising technology for the abatement of organic and non-biodegradable pollutants in wastewater. In order to better understand and improve the process, more cost-effective reactor configuration should be developed in future research.

# 3 Hybrid systems of RED and BESs for chemicals production and wastewater treatment

RED is an emerging technology for harvesting salinity gradient energy between two different concentration solutions. One normal RED stack generally comprises a series of CEMs and AEMs assembled in an alternating order. Anions and cations in high concentration solution transport to low concentration solution through CEM and AEM in opposite directions, the salinity gradient can be converted into electricity by the RED stack. In recent years, RED is becoming a possible option to store and capture salinity gradient energy (Hong et al., 2015; Mei & Tang, 2018). Considering the advantages and limitations of RED and BESs, a serious of hybrid systems of RED and BESs were explored. Based on the different structures and functions, the hybrid systems can be broadly classified into microbial reverse-electrodialysis cell (MRC) (Kim & Logan, 2011b), microbial reverse-electrodialysis electrolysis cells (MREC) (Kim & Logan, 2011a), microbial reverse-electrodialysis chemical production cell (MRCC) (Zhu et al., 2013), microbial reverse-electrodialysis electrolysis and chemical production cell (MRECC) (Zhu et al., 2014), and microbial reverse-electrodialysis methanogenesis cell (MRMC) (Luo et al., 2014), which can overcomes key limitations of individual system (Logan & Elimelech, 2012).

## 3.1 MRC for enhanced power production

MRC is a hybrid system of RED and MFC, which was developed to increase the voltage and power output (Logan & Elimelech, 2012). In MRC, a RED stack placed between anode and cathode. When five membrane-pairs RED stack was used in MRC for electricity generation, the maximum voltage (1.3V) substantially increased compared with those obtained with the MFC alone (0.5-0.6V). The power densities output by the MRC also were higher than that of individual systems. In addition, wastewater treatment can be accomplished in anode chamber of the MRC, the COD removal was ranging from 96 to 99% with anolyte pH decreased to 5.5 (Kim & Logan, 2011b). The COD removal rates could be greatly increased with wastewater in the anode chamber, the COD removal rate in MRC is nearly twice that of MFC (Cusick et al., 2013). The incorporation of thermolytic solution ($NH_4HCO_3$) into the MRC systems further increased the power density and eliminated the need of

natural water sources and reduced the capital cost of pre-treatment (Cusick et al., 2013; Cusick et al., 2012). Previous studies have proved that the MRC is an improved technology compared to individual MFC and RED systems. Furthermore, the MRC also provides a substantial and more efficient method to utilize salinity gradient energy and boost MFC voltage and power density output.

## 3.2 MRCC for acid and alkali production

One key limitation of the performance of MRC is that the anolyte pH would decrease to levels that inhibit microbial activity in the anode chamber. In order to avoid a significant decrease in the anolyte pH, Zhu et al. (2013) placed one bipolar membrane between the anode and the five membrane-pairs RED stack, which was named MRCC. In the MRCC, acid produced in the chamber between anode chamber and RED stack, alkali was produced in cathode chamber without external power supply. The anolyte pH was very stable, only has slightly decreased from 7 to 6.74. The MRCC offered one novel method of producing commodity chemicals (acid and alkali) using renewable salinity gradient energy and wastewater (Zhu et al., 2013).

## 3.3 MRECC for $H_2$ production and $CO_2$ sequestration

Base on MRCC, Zhu et al. (2014) further proposed a MRECC by placing one bipolar membrane between the anode and RED stack. In order to overcome the ohmic losses of the bipolar membrane and generate high potentials required to drive $H_2$ production, the number of cell pairs of RED stack was increased to seven. In this MRECC, RED stack as the power supply for acid and alkali solution production like MRCC, and $H_2$ also simultaneously produced in the cathode chamber. Compared to MRCC, the main advantage of the MRECC was substantially improved alkali solution production, which was suitable for $CO_2$ sequestration. The operating costs of the MRECC for $CO_2$ sequestration was approximately \$25/metric ton-$CO_2$, which is lower than that of other developed $CO_2$ sequestration technologies (more than \$65/metric ton-$CO_2$) (Zhu et al., 2014). So, the hybrid system of RED and MEC provide a strategy for chemicals production from $CO_2$, which might be a cost-effective and environmentally friendly technology.

## 3.4 MREC for $H_2$ production

Applied voltage is required by MEC to overcome the thermodynamic limit for $H_2$ production at the cathode (Logan et al., 2008). In order to eliminate the requirement of electrical grid energy, MREC was proposed by integrating one RED stack into MEC in 2011 (Kim & Logan, 2011a). In the MREC, the energy for driving $H_2$ production comes from the anodic exoelectrogens oxidize organic matters and the salinity gradient between seawater and river water. The most obvious advantage of MREC is $H_2$ can be produced on the cathode without external electrical energy supply, which is more efficiency than MEC on $H_2$ production (Nam et al., 2012; Song et al., 2016). However, the application of MREC was limited to coastal areas due to the requirement of river water and seawater. When use thermolytic solutions ($NH_4HCO_3$) replace the seawater and river water, the waste heat can be captured to dive $H_2$ generation (Luo et al., 2013). The use of thermolytic $NH_4HCO_3$ solutions in RED could enable energy capture from low grade waste heat, that because the $NH_4HCO_3$ solution can be regenerated through conventional distillation technologies and waste heat (~60 ℃). Although MREC has great potential for various purposes, many works still should be done to improve its performance before practical use. Furthermore, the application range of MREC also should be extended.

## 3.5 MRMC for $CH_4$ production

The production of $H_2$ in MREC in situ may be used to react with $CO_2$ and produce high valuable products. Following the same strategies, the MREC with methanogenic bio-cathode was proposed for methane production, which also was called MRMC (Luo et al., 2014). In this MRMC, the maximum methane production rate could reach to $2.3 \pm 0.1$ mmol $L^{-1}$ $day^{-1}$. However, the energy efficiency obtained in MRMC for methane production is relatively low than that of MREC for $H_2$ production. Moreover, the peak current of MRMC (1.0-1.5 mA) for methane production also was lower than that of MREC (3.2 mA) for $H_2$ production. The energy efficiency and current of MRMC should be enhanced for methane production.

## 3.6 MREC for $H_2O_2$ production

Previous studies have demonstrated the MEC is a promising method to produce $H_2O_2$ (detail see chapter 2). However, the external power source required by MEC may add the costs to the process and hinder its practical application. In addition, MREC is more efficient than MEC on energy capture.

In this context, the feasibility of MREC on $H_2O_2$ production was assessed in **Paper II**. This structure of MREC for $H_2O_2$ production is different with conventional MREC for $H_2$ production, which consisted of anaerobic anode chamber, RED stack and aerobic cathode chamber (**Figure 7**). High concentration NaCl solution as synthetic seawater (HC) and low concentration NaCl solution as synthetic river water (LC) flow into the RED stack.

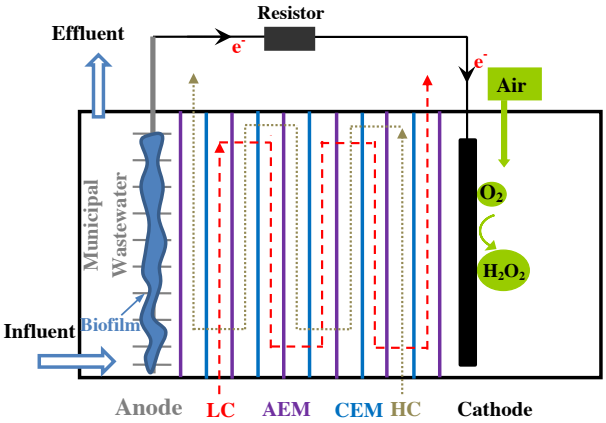


**Figure 6.** Schematic diagram of MREC for $H_2O_2$ production. (CEM: cation exchange membrane, AEM: anion exchange membrane, HC: high concentration solution, LC: low concentration solution) (**Paper II**)

In general, the $H_2O_2$ generation and self-decomposition reaction occur simultaneity on the surface of cathode during electrosynthesis process. As mentioned in Chapter 2, the cathode potential is the main factor for $H_2O_2$ generation. The optimal cathode potential for $H_2O_2$ production was different in different MEC studies. For instance, Sim et al. find the maximum $H_2O_2$ yield was achieved at cathode potential of -0.4 V (Sim et al., 2015b). However, Li et al. (2016a) observed that the optimal cathode potential is -1.4 V for $H_2O_2$ production in their MEC. The cathode potential can be controlled at suitable value by using external power source or potentiostat in MECs. However, the MREC is operated without external power source, the control of cathode potential at optimal value for effective $H_2O_2$ generation could be one challenge.

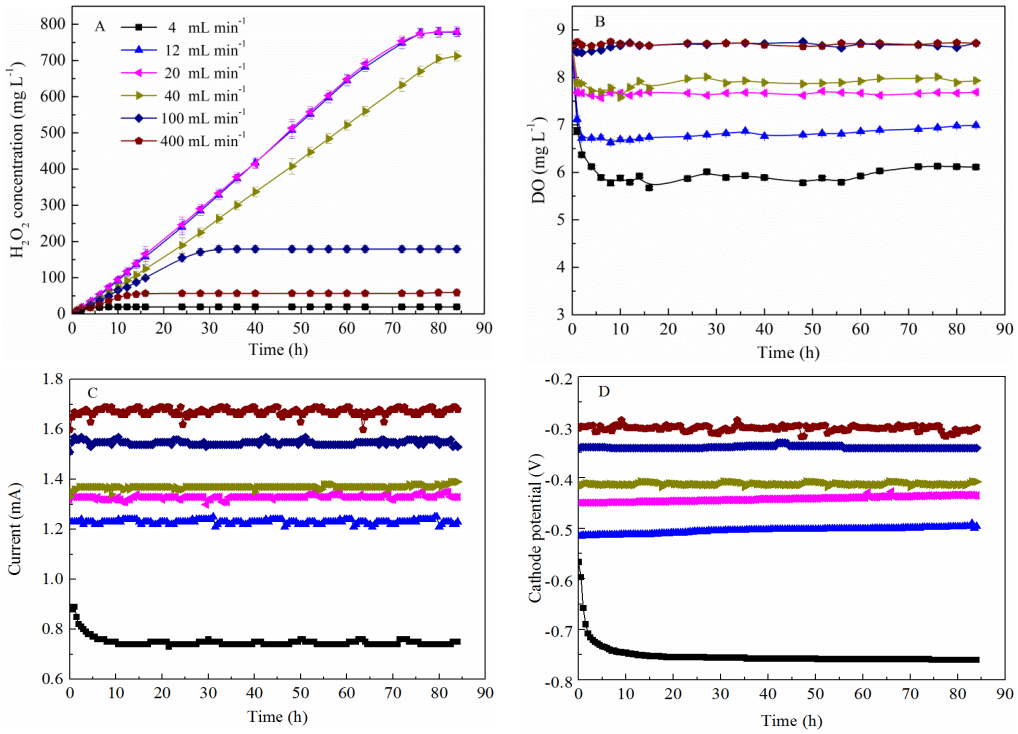


**Figure 7.** The effect of air flow rate on the concentration of $H_2O_2$ (A), DO (B), Current (C) and Cathode potential (D) (**Paper II**).

As mentioned in Chapter 2, the air flow rate also is an important impact on $H_2O_2$ production in MREC. For instance, the corresponding $H_2O_2$ concentration could increase from 19 ± 2.5 to 778 ± 11 mg $L^{-1}$ with the air flow rate from 4 to 20 mL $min^{-1}$ (Figure. 7A). When the air flow rate increased above 40 mL $min^{-1}$, the $H_2O_2$ concentration started to decrease. Further increase the air flow rate to 400 mL $min^{-1}$, the $H_2O_2$ concentration only was 59 ± 10 mg $L^{-1}$. It is generally considered that a higher $O_2$ flow rate is beneficial for $H_2O_2$ generation, since high air flow rate could enhance the dissolved oxygen in the catholyte (Figure 7B) and promote the mass transfer rate, which is helpful for the $H_2O_2$ accumulation in $H_2O_2$ electro-generation process (Yu et al., 2015a; Yu et al., 2015b). However, excessive air supply could disturb the mass transfer between catholyte and electrode and result in low $H_2O_2$ accumulation concentration (Luo et al., 2015).

The air flow rate also could affect the cathode potential and current (Figure 7C and D) of MREC. The cathode potential becomes less negative and the current increased with the increase of air flow rate. The maximal current (1.68 ± 0.03 mA) and the cathode potential of -0.310 ± 0.05 mV were achieved with the air flow rate of 400 mL $min^{-1}$. However, the optimal air flow rate for $H_2O_2$ production is in the range of 12 to 20 mL $min^{-1}$, the corresponding cathode potential was ranging from -0.505 ± 0.005 to -0.442 ±

0.006 V. Optimal air flow rate is necessary for $H_2O_2$ production in the MREC.

Besides, another key challenge of the MREC is that a large amount of sea-water and river-water are required (Logan & Elimelech, 2012; Luo et al., 2013). To make the MREC an economically attractive technology, the sea-water and river water should be recycled. The concentration of HC solution decreased with the increasing of recycle time, while the concentration of LC solution showed opposite trend. The salinity ratios between HC and LC solutions became smaller and smaller (Figure 8A). The $H_2O_2$ concentration and current started to decrease after 9 cycles. However, the cathode potential began to increase (Figure 8B). A possible explanation could be that the decreasing of salinity ratio decreased electrochemical junction potential in the RED stack (Nam et al., 2012).

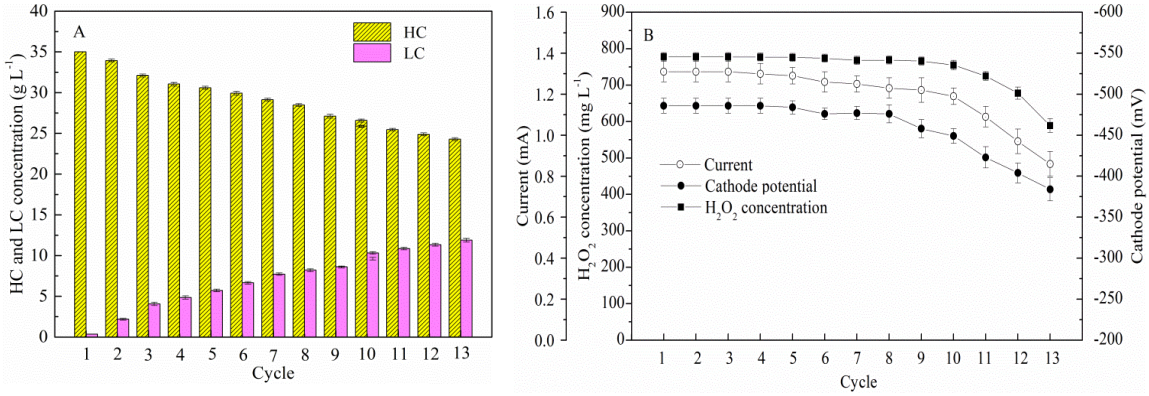


**Figure 8**. The effect of HC and LC concentration on $H_2O_2$ generation (**Paper II**).

In the light of $H_2O_2$ production and the electrical energy consumption (detail see **Paper II**), the energy input (0.45 ± 0.03 kWh $kg^{-1}$ $H_2O_2$) was significantly lower than that of MECs (0.66~0.93 kWh $kg^{-1}$ $H_2O_2$) (Rozendal et al., 2009) and Electro-synthesis processes (6.0~22.1 kWh $kg^{-1}$ $H_2O_2$) for $H_2O_2$ production (Yu et al., 2015b). Moreover, the domestic wastewater was treated efficiently in the anode chamber. The low energy cost for $H_2O_2$ production and simultaneous wastewater treatment make the MREC technology more promising than MECs and Electro-synthesis processes.

## 3.7 MREC-Fenton system for azo dyes removal

MREC as a novel hybrid BES has been demonstrated as an efficient platform technology for wastewater treatment in the anode chamber and $H_2$ or $CH_4$ production in the cathode chamber without external power supply (Luo et al., 2013; Luo et al., 2014). In MREC, the electric energy generated by the exo-electrogens and salinity-gradient between different concentration solutions

(e.g., seawater and river water) could be utilized to drive the $H_2O_2$ production with low electrical energy consumption (**Paper II**). Therefore, integrating the MREC and Fenton process could be an economical and efficient BEF technology to degrade bio-refractory pollutants in cathode chamber, which was named MREC-Fenton system in **Paper III**. The laboratory scale MREC-Fenton system was conducted as shown in Figure 9. This system holds great potential as sustainable method to remove biodegradable pollutants in anode chamber and degrade bio-refractory pollutants in cathode chamber without any external power supply by integrating Fenton process. Orange G, a typical azo dye, was selected as the target pollutant due to its wide use in dyeing the textile fabric and strong toxic influence to human and environment (Cai et al., 2016a; Pereira et al., 2016). Details of the configuration and operation of MREC-Fenton system, analytical methods are described in **Paper III**. The cost of treating Orange G wastewater is 25.93 kWh $kg^{-1}$-TOC, which is much lower than that of conventional Electro-Fenton process with a cost of 45.8-865 kWh $kg^{-1}$-TOC (Gao et al., 2015; Xu et al., 2008). The key advantage of MREC-Fenton system is the replacement of electricity energy from power grid with renewable salinity-gradient energy that was captured in RED to directly drive the Fenton process. Due to that cathode and anode chamber are completely separated with RED stack, the continuous flow mode of wastewater in anode chamber does not affect the Fenton process in cathode chamber.

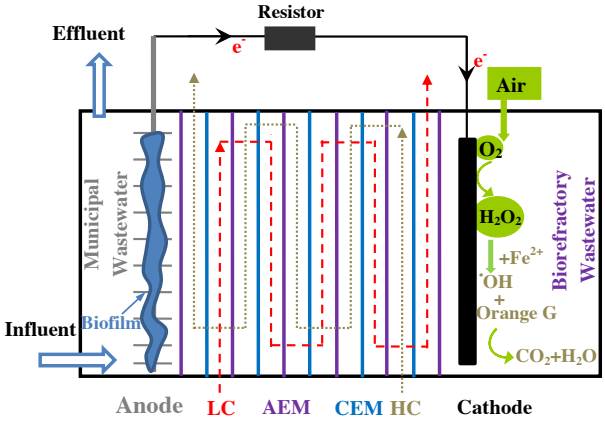


**Figure 9.** Schematic diagram of MREC-Fenton system for Orange G degradation. (CEM: cation exchange membrane, AEM: anion exchange membrane, HC: 35 g $L^{-1}$ NaCl solution, LC: 0.35 g $L^{-1}$ NaCl solution) (**Paper III**).

The degradation of Orange G in MREC-Fenton system was significantly influenced by wastewater pH. The highest degradation rate of Orange G was found at pH 2. The degradation efficiency could reach 100% when the Orange G concentration in the range of 100-400 mg $L^{-1}$ with the Orange G

wastewater initial pH was set at 2. During the degradation of Orange G, the decolorization rate was higher than the mineralization rate. That is because the Orange G also is one strong electron acceptor, which can be decomposed into colorless shorter organic molecules by electrochemical function (Pereira et al., 2016). In addition, acidic environment also is a benefit for the cleavage of azo bond, the azo bond would be first cleaved by the $^{\bullet}OH$, resulting in the formation of colorless organic molecules. This behavior was in line with the conventional Electro-Fenton process for Orange G degradation (Cai et al., 2016a; Cai et al., 2016b).

HC and LC solutions flow rate and air flow rate are the key operating parameters of MREC. When the HC and LC flow rate were set at 0.2-1.5 mL $min^{-1}$ and the air flow rate was set at 4-32 mL $min^{-1}$, the degradation efficiency of Orange G (400 mg $L^{-1}$) could reach 100%. The energy consumption of pumping HC and LC solutions is the key costs for MREC operation (Zhu et al., 2015). Thus, considering the degradation efficiency of Orange G and energy consumption of pumping, the optimal solutions flow rate should be at 0.5 mL $min^{-1}$. The decolorization rate and mineralization rate also were influenced by the air flow rate when HC and LC solutions flow rate was fixed at 0.5 mL $min^{-1}$. The apparent decolorization constant ($K_{app}$) and mineralization rate constant ($K_{TOC}$) increased with air flow rate and reached the maximum at 16 mL $min^{-1}$ (Figure 10).

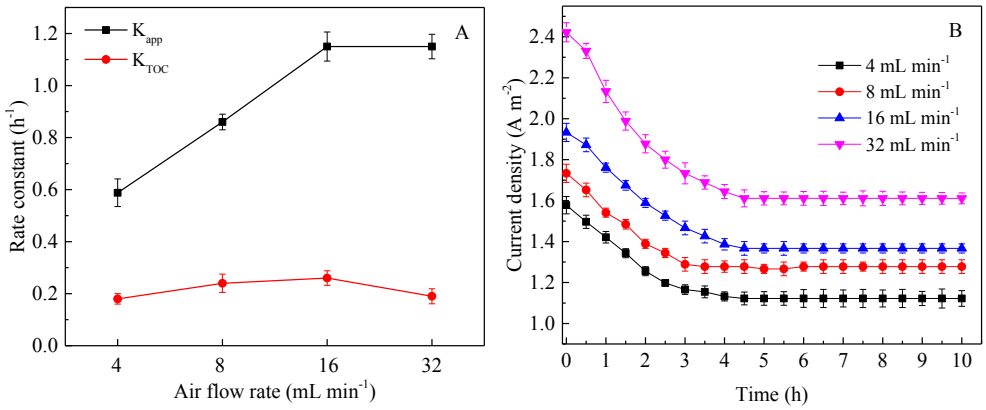


**Figure 10.** The influence of air flow rate on the Orange G degradation in the MREC-Fenton system. Experiment conditions: Orange G concentration of 400 mg $L^{-1}$, initial pH 2, $Fe^{2+}$ of 10 mM, HC and LC solutions flow rate of 0.5 mL $min^{-1}$ (**Paper III**).

# 4 BESs for fixing $CO_2$ into value-added chemicals and wastewater treatment

In order to balance the increasing energy demand with the need to economically reduce $CO_2$ emissions, cost-effective and efficient $CO_2$ capture and conversion technologies are highly desired. MES is progressed as a new perspective for converting the greenhouse gas $CO_2$ into high value chemicals and biofuels using some special microorganisms (e.g., *Sporomusa* ovata, *Clostridum Ljungdahlii*) as biocatalysts on cathode (Aryal et al., 2017b; Rosenbaum & Henrich, 2014). In recent years, the main focus in MES microbiology research was on finding new electrosynthesis microorganisms, modifying and optimizing electrosynthesis microorganisms for target applications (Schlager et al., 2017). The most well studied electrosynthesis microorganisms are *Sporomusa* ovata and *Clostridum Ljungdahlii*. The *C*. *Ljungdahlii* is the most intensively researched synthesis microorganism for $CO_2$ conversion to a range of fatty acids and alcohols. The best of electrosynthesis microorganism is *S*. ovata, which was reported to produce acetate from $CO_2$ with cathode potential at -400 mV versus standard hydrogen electrode (Aryal et al., 2017b). Electron recovery in acetate and by-products was more than 85% (Rosenbaum & Henrich, 2014). The acetate was synthesized through two routes (route 1 and 2) using *S*. *ovata* as inoculum in MES system. The route 1 mainly occurred in MES with biofilm on the cathode, where microbial cells gain electrons from the cathode and convert $CO_2$ to acetate or other chemicals (Kadier et al., 2016; Rabaey & Rozendal, 2010). In route 2, electrons were transferred from the cathode to *S*. *ovata* via molecular $H_2$, which can be in situ generated and thereby facilitating the rate and yield of acetate generation (Blanchet et al., 2015; May et al., 2016). More recently, Zhang et al. (2016) reported the *S*. *ovata* can convert the $CO_2$ to acetate and ethanol by modifying the cultivation medium in MES.

Route 1:

$$2\,CO_2 + 8\,H^+ + 8\,e^- \rightarrow CH_3COOH + 2\,H_2O$$

Route 2:

$$2H^+ + 2\,e^- \rightarrow H_2$$

$$2\,CO_2 + 4\,H_2 \rightarrow CH_3COOH + 2H_2O$$

Since 2010, the performance of MES has been improved by optimizing cathode material, reactor design and biocatalysts (Aryal et al., 2017a; Nevin et al., 2010; Tremblay et al., 2017). Biocatalysts have been improved successfully by pure culture and mixture culture in the laboratory (May et al., 2016). A serious of cathode materials also have been explored to improve the productivity of MES (Aryal et al., 2017a). The MES reactor design and configuration directly affect the performance of $CO_2$ reduction and value-added chemicals production. In the past years, several different types of MES reactor configurations have been designed in lab-scale studies, such as conventional two chambers MES system, MEC-based MES system, photo-MES system and membraneless MES (Tremblay et al., 2017). They are operated under different operation conditions to enhance the performance and reduce the cost of MES. However, in order to make MES more commercial, developing more cost-effectiveness MES reactor architecture is needed (Tremblay et al., 2017).

## 4.1 A novel MES system for $CO_2$ reduction

In this current study, a novel MREC system was proposed for acetate and ethanol production from $CO_2$ reduction. This MREC system was renamed as microbial reverse-electrodialysis synthesis cell (MRESC) to highlight its new application. This MRESC consisted of anode and cathode chamber, which were separated by one RED stack (Figure 11). The RED stack comprised five cell pairs, each consisting of a couple of AEM and CEM, high concentration NaCl solution as synthetic seawater (HC) and low concentration NaCl solution as synthetic fresh water (LC) flowed in the RED stack. The anode chamber of MRESC was continuously fed with domestic wastewater. The cathode chamber was operated in batch mode. The catholyte was circulated over a recirculation bottle of 250 mL with a peristaltic pump at 10 mL $min^{-1}$. The cathode chamber was continually bubbled through a diffuser with $CO_2$, pumped by a peristaltic pump. The effluent gas from the cathode chamber was collected in a gas bag.

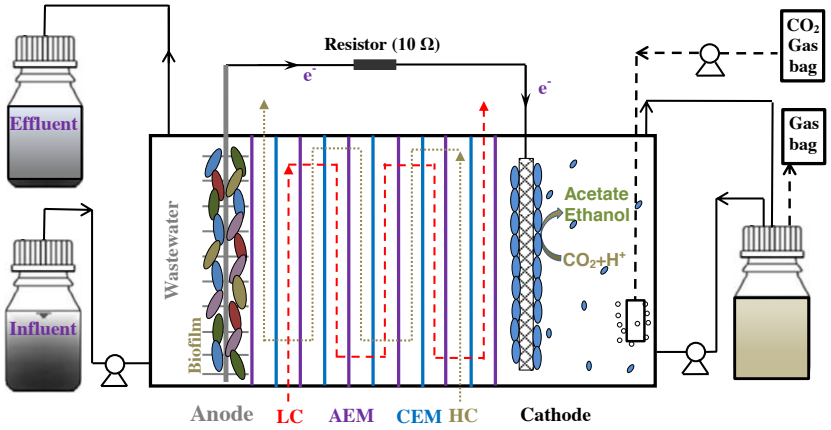


**Figure 11.** Schematic of MRESC system. (CEM: cation exchange membrane, AEM: anion exchange membrane, HC: high concentration NaCl solution, LC: low concentration NaCl solution) (**Paper IV**).

*Sporomusa ovata* (DSM-2662) is one of the most efficient species for MES (Aryal et al., 2017b). In **paper IV**, the *S. ovata* was cultured in the growth medium (DSMZ 311 omitting betaine, fructose, casitone and resazurin) under $H_2$: $CO_2$ (80:20) atmosphere. Subsequently, *S. ovata* was cultured for three generations in modified phosphate buffer-enhanced growth medium under $H_2$: $CO_2$ (80:20) atmosphere. The pre-cultivated *S. ovata* were used as inoculum source in the MRESC system. The medium for MRESC experiments was modified phosphate buffer-enhanced growth medium with different phosphate concentration as shown in **Paper IV**.

## 4.2 The performance of MRESC system

The acetate concentration could reach to 439.8 ± 21.5 mg $L^{-1}$ in the MRESC system (Figure 12). Ethanol was synthesized as by-product, its maximum concentration was only 39.1± 8.5 mg $L^{-1}$. Four control experiments were carried out in which current (open circuit), *S. ovata*, salinity gradient and exoelectrogenic microorganisms were omitted. No acetate and ethanol were generated under the conditions of open circuit (Control 1), without inoculation of *S. ovata* (Control 2) and no salinity gradient (Control 3). Only 85.6 ± 11.9 mg $L^{-1}$ of acetate was produced without microorganisms at anode (Control 4). These results demonstrated the productivity of MRESC on the conversion of $CO_2$ to acetate and ethanol. The mechanism of $CO_2$ reduction at the cathode is the Wood-Ljungdahl pathway, which is similar with conventional MES system (Ammam et al., 2016; Blanchet et al., 2015).

The *S. ovata* could enhance the flow of electrons at the cathode, resulting in the increasing of current. For instance, the current (2.7 ± 0.1 mA) of MRESC

system was higher than that without inoculation of *S. ovata* (control 2). The COD removal efficiency in anode chamber reached 85.26 ± 0.88%. On the basis of COD removal, the coulombic efficiency of MRESC was 37.82 ± 0.98%. The recovery of electrons in acetate was 75.94 ± 3.73%, which is close to that of the conventional MES systems using *S. ovata* as biocatalyst (71-93%) (Aryal et al., 2016; Zhang et al., 2013).

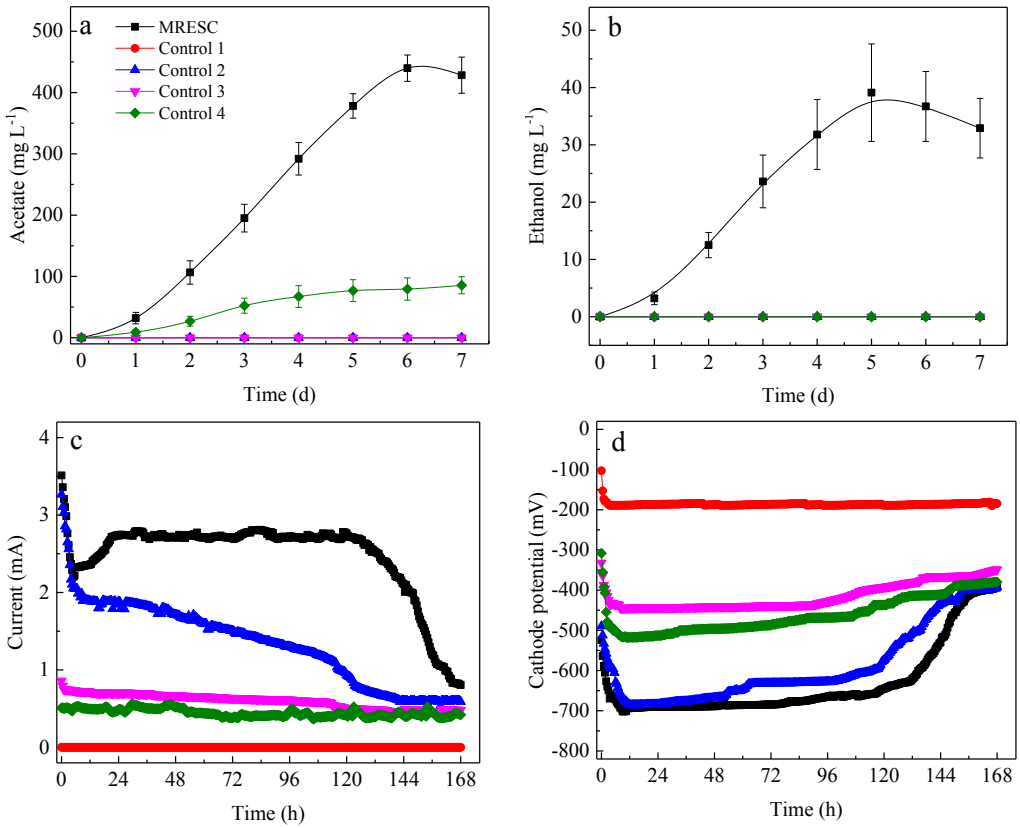


**Figure** 12. The performance of MRESC on the conversion of $CO_2$ to acetate and ethanol. (MRESC: HC and LC flow rate of 0.5 mL $min^{-1}$, $CO_2$ flow rate of 550 mL $d^{-1}$; Control 1：open circuit; Control 2: without inoculation of *S. ovata*; Control 3: no $CO_2$ bubbled in cathode chamber of MRESC; Control 4: without exoelectrogenic microorganisms on the anode. All the cathode potentials were vs. Ag/AgCl reference electrode) (**Paper IV**).

### 4.2.1 The influence of operation parameters on system performance

The performance of MRESC system was significantly influenced by the key operation parameters, such as HC and LC solutions flow rate, $CO_2$ flow rate and phosphate buffer concentration. In the MRECS system, when the flow rate of HC and LC solutions was changed from 0.1 to 0.5 mL $min^{-1}$, the current of MRESC increased from 1.1 ± 0.09 to 2.7 ± 0.1 mA. The increase of current is beneficial for microbial conversion of $CO_2$ to acetate (Aryal et al., 2016). So, the acetate concentration increased from 133.3 ± 19.7 to 439.8 ±

21.5 mg $L^{-1}$. Further increase the flow rate to 1.5 mL $min^{-1}$, the acetate production was not further improved with the flow rate. Other factors would limit the MRESC system performance. Thus, 0.5 mL $min^{-1}$ was considered as the optimal HC and LC solutions flow rate.

The $CO_2$ as the substrate for chemicals production in MES, its flow rate could significantly influence the production rate of the products and the consumption rate of $CO_2$ (Jourdin et al., 2015; Patil et al., 2015). For instance, when the $CO_2$ flow rate was set at 280 mL $d^{-1}$, the maximum acetate concentration only was 236.7 ± 28.3 mg $L^{-1}$. Further increase the $CO_2$ flow rate to 550 and 1100 mL $d^{-1}$, the acetate concentration was stabilized at maximum (439.8 ± 21.5 mg $L^{-1}$). In addition, based on the carbon balance, only 2.47 ± 0.12% of supplied $CO_2$ was converted to acetate and ethanol.

The cultivation medium has a direct influence on the capacity of *S. ovata* (Ammam et al., 2016). Phosphate-enhanced medium could enhance the acetate production in *S. ovata* electrosynthetic process (Liu et al., 2015). There are two possibilities to explain the influence of phosphate buffer. First, the phosphate buffer can prevent medium pH increasing in cathode that is benefit for the growth of *S. ovata*. Secondly, the addition of phosphate buffer can enhance the conductivity of the cultivation medium, which will decrease the resistance of the medium. However, exorbitant buffer concentration will inhibit the *S. ovata* growth. For instance, the acetate concentration increased from 28.6 ± 5.9 to 477.5 ± 33.2 mg $L^{-1}$ with the increasing of buffer concentration from 0 to 100 mM. However, when the buffer concentration further increased to 200 mM, the acetate concentration decreased to 365.7 ± 24.3 mg $L^{-1}$.

### 4.2.2 The wastewater treatment in MRESC system

The highest COD removal from domestic wastewater in the anode chamber could reach to 91.15 ± 0.96%. Moreover, the treatment performance of wastewater in anode chamber of MRESC was not affected by the HC and LC solutions flow rate, $CO_2$ flow rate, phosphate buffer concentration. As the anodic microorganisms of MRESC system could use various kinds of organic waste, such as municipal wastewaters and animal wastewaters. Therefore, the MRESC system should be one promising wastewater treatment biotechnology with simultaneous chemicals production from $CO_2$ reduction.

## 4.3 The advantages of MRESC system

MES systems need electrical energy to supply electrons and control biocathode potential for $CO_2$ conversion (Aryal et al., 2017a; Rabaey & Rozendal, 2010; Tremblay et al., 2017). The external power supply adds significant costs to the process, especially for a long-term commercial application (Bajracharya et al., 2017; ElMekawy et al., 2016; Marshall et al., 2013). Previous studies have demonstrated that the overall costs of MES should be further reduced in order to be economically competitive and environmentally sustainable (Christodoulou et al., 2017). Renewable power sources such as solar energy and wind power can be potentially used to make the MES a more green and sustainable technology for $CO_2$ conversion (Ammam et al., 2016; Liu et al., 2015). However, the widespread utilization of these renewable energy sources is limited by their fluctuating and intermittent characteristic (Gao et al., 2017; Nevin et al., 2010). No strategy to directly convert $CO_2$ to value-added chemicals in MES process without an external power source was proposed. Salinity gradient energy as a remarkable green energy can be directly converted into electrical power by using RED (Ramon et al., 2011; Zhu et al., 2017). In addition, the salinity gradient energy is abundant and can be found in various environments, such as in the seawater and river water, or desalination brine and low salinity effluents from wastewater treatment (Logan & Elimelech, 2012), or waste heat and thermolytic streams (Cusick et al., 2012). In this context, the MRESC will be a cost-effective and efficient BES technology for conversion of $CO_2$ to value-added chemicals (e.g., acetate and alcohol).

# 5 Conclusions

This thesis focused on the development of effective and environmentally friendly BES for valuable chemicals production and wastewater treatment. The major contributions resulting of this thesis are summarised below:

- The bipolar membrane MEC-Fenton system as an effective and environmentally friendly technology for aniline containing wastewater treatment was proved. In such system, real aniline wastewater was effectively treated with aniline removal efficiency of 97.1 ± 1.2%.
- In MEC-Fenton system, bipolar membrane could be used to help sustaining a low catholyte pH without the need of extra acid dosage during the operating period.
- The electrical energy consumption only was 1.423 kWh $kg^{-1}$-TOC by using MEC-Fenton system to treat real aniline wastewater. The MEC-Fenton system with bipolar membrane would provide a cost-effective and applicable for efficient treatment of bio-refractory wastewater.
- The MREC system is an attractive method for $H_2O_2$ production. In the MREC, high $H_2O_2$ concentration could reach to 778 ± 11 mg $L^{-1}$ without utilizing external power source. The energy costs for $H_2O_2$ production was as low as 0.45 ± 0.03 kWh $kg^{-1}$ $H_2O_2$.
- Due to the unique advantages of MREC for harvesting energy from salinity gradient and $H_2O_2$ production, high removal rate of azo dye (Orange G) can be achieved without external power supply through integrating Fenton process. The MREC-Fenton system provides a novel platform technology for bio-refractory wastewater treatment.
- An innovative MREC system was developed to convert $CO_2$-to-acetate and ethanol and simultaneously treat wastewater by using the salinity-gradient energy as power source, which was renamed MRESC. The COD removal of the domestic wastewater was not affected substantially by the HC and LC solutions flow rate, $CO_2$ flow rate, phosphate concentration and salinity gradient.
- The MRESC is not only a novel method for simultaneous production of biofuels and wastewater treatment, but also offers a novel MES technology for salinity gradient energy harvesting and storage and $CO_2$ sequestration.

- The MRESC system established a starting point for conversion of $CO_2$ to a variety of value-added chemicals (e.g., multi-carbon molecules) upon the choice of biocatalysts for the synthesis.
- In MREC and MRESC system, high COD removal ($\geq$ 85%) in the anode chamber was obtained which may enable effective wastewater treatment in addition to valuable chemicals production. The current study demonstrated the hybrid system of RED and BES could be a potential method for wastewater treatment in the anode chamber, although post treatment still is needed.

# 6 Future research

The present PhD study developed several novel and cost-efficient BESs to improve the performance of value added chemicals production ($H_2O_2$ and acetate) and wastewater treatment. However, there still remain some challenges in the study and further studies are also needed as following:

- The current studies of MEC-Fenton systems only focus on basic application and reactor design in laboratory. As a new technology, it is still facing some challenges. The energy recovery and pollutants removal rate still need to be further improved to make MEC-Fenton system more efficient and competitive technology. Moreover, more cost-effective reactor configuration and large-scale operation could be the interest of further research for commercial application.
- Due to the chemical components of most real wastewaters are very complex, the MEC-Fenton system should be extensively studied with various real industrial wastewaters. The kinetic modeling also should be proposed in future research, which can provide some important fundamental knowledge for the further use in practical applications.
- The MREC-Fenton system has potential to remove many bio-refractory pollutants in cathode chamber. However, the TOC removal rate was low. In order to improve the TOC removal rate, more efficient MREC reactor configuration should be exploited in future research. Polite-scale MREC-system with continuous operation should be developed in order to validate the system at commercial scale conditions.
- In order to make MREC more economical during the conversion of $CO_2$ to value-added chemicals, future examinations on MREC need to focus on the systems up-scaling. Furthermore, in next-generation designs, higher efficiencies should be enhanced through improvement of peripheral limitations such as $CO_2$ mass transport in the electrolyte, cathode material and reactor structure. Especially, the application of commercial RED would observably reduce the cost and increase the production rate and product yield.

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# 8 Papers

**I** **Li, X.,** Jin, X., Zhao, N., Angelidaki, I., Zhang, Y. 2017. Efficient treatment of aniline containing wastewater in bipolar membrane microbial electrolysis cell-Fenton system. Water Research, 119, 67-72.

**II** **Li, X.,** Angelidaki, I., Zhang, Y. 2017. Salinity-gradient energy driven microbial electrosynthesis of hydrogen peroxide. Journal of Power Sources, 341, 357-365.

**III** **Li, X.,** Jin, X., Zhao, N., Angelidaki, I., Zhang, Y. 2017. Novel bio-electro-Fenton technology for azo dye wastewater treatment using microbial reverse-electrodialysis electrolysis cell. Bioresource Technology, 228, 322-329.

**IV** **Li, X.,** Angelidaki, I., Zhang, Y. Salinity-gradient energy driven microbial electrosynthesis of value-added chemicals from $CO_2$ reduction. Submitted.

**V** **Li, X.,** Chen, S., Angelidaki, I., Zhang, Y. Bio-Electro-Fenton processes for wastewater treatment: advances and prospects. Submitted.

In this online version of the thesis, **paper I-V** are not included but can be obtained from electronic article databases e.g. via www.orbit.dtu.dk or on request from.

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The department dates back to 1865, when Ludvig August Colding, the founder of the department, gave the first lecture on sanitary engineering as response to the cholera epidemics in Copenhagen in the late 1800s.

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